REMOVAL OF ESTERIFICATION CATALYST BY SEPARATION

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Removal of esterification catalyst by separation

The present invention relates to a process for removal of the
5 esterification catalyst by separation from a crude plasticizer
ester obtained by reacting a dicarboxylic acid with C_8–C_{13}
alcohols, by treating the crude ester with an aqueous alkali
solution in the range from 10 to 100°C and then separating the
aqueous alkaline phase comprising the hydrolyzed esterification
10 catalyst by gravitational phase separation.

Phthalic diesters and adipic diesters are important plasticizers
for plastics, in particular PVC. When these diesters are produced
industrially, the usual method is to react phthalic anhydride or
15 adipic acid with approximately twice the molar amount of an
alcohol in the presence of an esterification catalyst. Important
members of the resultant class of phthalic diesters and adipic
diesters are the dialkyl esters, derived from the corresponding
alcohols, such as octanols or nonanols. The esterification
20 catalysts mostly used nowadays are Lewis-acid salts of elements
of the 4th main group or the 4th transition group of the Periodic
Table of the Elements.

At the end of the esterification reaction, the esterification
25 catalyst is normally destroyed by adding alkali. Practical
considerations means that the materials mostly used for this
purpose are aqueous solutions of an alkali metal hydroxide or of
an alkali metal carbonate. The hydrolysis products of the
esterification catalyst are mainly in the aqueous phase after
30 catalyst destruction, and that phase is then removed by
separation.

However, a difficulty mostly arising with the separation of
organic product phase and alkaline aqueous phase under practical
35 conditions is that an emulsion layer forms between the two phases
to be separated after catalyst destruction.

It has now been found that this emulsion layer comprises
hydrolysis products of the catalyst, and also alkali metal salts
40 of half-esters made from one mol of dicarboxylic acid and one mol
of esterification alcohol (the term "half-ester" being used for
these below). The emulsion layer frequently also comprises
considerable amounts of diester.

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The half-esters derive firstly from incomplete conversion of the monoester by the esterification alcohol. Secondly, they can also be produced from diester by alkaline hydrolysis during the destruction of the esterification catalyst by alkali.

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These emulsions cannot generally be broken in conventional separators using prolonged residence times. A consequence of this is that the emulsions often pass to some extent into the organic phase during phase separation and, when this phase is worked up,
10 cause undesirable deposits in the downstream sections of the plasticizer-production plant. Some of the emulsion can also be separated out with the aqueous phase, causing product losses.

It has therefore been desirable to find a process for "breaking"
15 these emulsions prior to phase separation.

The use of chemical means for this purpose is known to the skilled worker.

20 For example, DE-A 23 18 657 describes the two-stage destruction of an oil-in-water emulsion by using $FeCl_3$ or $AlCl_3$ to adjust to a pH of from 2 to 3. Immediately following this, NaOH or $Ca(OH)_2$ is used for neutralization.

25 The Czechs patent CS 274812 also proposes a two-stage process, in which the emulsion is first acidified and then treated with a polyvalent salt, such as $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ or $FeCl_3$.

A precondition for each of these known processes is therefore
30 that the emulsion to be broken has a pH markedly below 7 (acid range).

When applied to the present technical problem, namely the destruction of an emulsion at the interface between an organic
35 product phase and an alkaline aqueous phase of a crude esterification product, these known processes are inconvenient and not cost-effective.

It is an object of the present invention, therefore, to provide a
40 process which is simpler and more cost-effective to carry out for the destruction of these emulsions arising during the alkaline aqueous hydrolysis of the catalysts in the abovementioned preparation processes for dicarboxylic diesters.

45 We have found that this object is achieved by means of a process for removal of the esterification catalyst by separation from a crude plasticizer ester obtained by reacting a dicarboxylic acid

with C_8-C_{13} alcohols, by treating the crude ester with an aqueous alkali solution in the range from 10 to 100°C and then separating the aqueous alkaline phase comprising the hydrolyzed esterification catalyst by gravitational phase separation, which
5 comprises treating the crude ester, prior to or during the phase separation, with a salt of a di- or polyvalent metal, or with a mixture of these salts.

The dicarboxylic acids used may be aromatic or aliphatic organic
10 dicarboxylic acids preferably having from 3 to 12 carbon atoms. Particular preference is given to dicarboxylic acids of this type having from 6 to 8 carbon atoms, such as adipic acid and phthalic acid. Instead of the dicarboxylic acids, it is also possible to use their derivatives which are generally more reactive in
15 esterification reactions, for example phthalic anhydride in the case of phthalic acid, or the acid dichlorides.

The esterification alcohols preferably used are monoalcohols having from 6 to 13 carbon atoms. Particular preference is given
20 to branched or unbranched monoalcohols, or mixtures of branched and unbranched monoalcohols, having from 8 to 11 carbon atoms.

The process of the invention is particularly suitable for the destruction of emulsions arising during the preparation of di-C_8
25 phthalates, di-C_9 phthalates, di-C_{10} phthalates, di-C_8 adipates, di-C_9 adipates, and di-C_{10} adipates.

As esterification catalyst, preference is given to a Lewis-acid compound of an element of the 4th main group or of the 4th
30 transition group of the Periodic Table of the Elements.

Preferred esterification catalyst metals are tin, antimony, titanium, or zirconium, titanium being particularly preferred.

35 Preferred esterification catalysts are the halides, alkoxylates, and alkoxycarbonylates of the esterification-catalyst metals, for example $TiCl_4$, $ZrCl_2(O\text{-ethyl})_2$, $ZrOCl_2$; particular preference is given to the titanium alkoxylates, and in particular $Ti(O\text{-ethyl})_4$, $Ti(O\text{-isopropyl})_4$, $Ti(O\text{-isobutyl})_4$.
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The amount used of the esterification catalyst, based on the dicarboxylic acid to be esterified or, where appropriate, on the derivative of the dicarboxylic acid, is generally from 0.001 to 0.8% by weight, preferably from 0.01 to 0.08% by weight.
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Other aspects of the preparation of the dicarboxylic diesters using these esterification catalysts are quite familiar to the person skilled in the art (cf., for example, DE-A 1 945 359), and it is therefore unnecessary to give further details in this
5 connection.

Completion of the reaction of the dicarboxylic acid with the esterification alcohol in the presence of the esterification catalyst generally gives a homogeneous solution of the
10 esterification catalyst in the crude product mixture, mainly composed of diester.

To destroy the esterification catalyst, the product mixture is generally treated with a from 2 to 10% strength by weight aqueous
15 alkali solution, such as sodium hydroxide solution, or with an aqueous solution of potassium carbonate and water. The method of operation here is normally that the final phase ratio of the aqueous phase to the organic phase is in the range from 0.1 : 1 to 10 : 1 parts by weight.
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Based on a volume of 1 liter of the aqueous phase, from 0.05 to 30 mmol of a salt of a di- or polyvalent metal or of a mixture of these salts is added to the resultant two-phase system composed of organic product phase and aqueous phase.
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Preferred salts used for the process of the invention are: halides, sulfates, mixed halide sulfates, and ternary alkali metal halides/sulfates of iron, aluminum, and calcium, for example sulfates such as aluminum sulfates, e.g. $Al_2(SO_4)_3$, iron
30 sulfate, e.g. $Fe_2(SO_4)_3$, chlorides such as aluminum chloride, iron(III) chloride, potassium aluminum sulfates such as $KAl(SO_4)_2$, calcium salts such as calcium oxide and calcium chloride. Particular preference is given to calcium salts and aluminum salts, and among these very particular preference is given to the
35 aluminum salts.

The form in which the salt or the mixture of salts is added may be that of a solution, preferably in water, or a solid.

40 In one preferred embodiment of the process of the invention, the salt or the mixture of the salts is added to the crude ester during the alkali treatment and/or during any washing carried out.

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The metal salt solution reaction is generally carried out at from 10 to 120°C, preferably from 40 to 90°C, and at a pressure of from 0.5 to 4 bar, preferably at atmospheric pressure.

5 The process of the invention may be carried out continuously or batchwise, and it is generally particularly cost-effective here to operate continuously where the destruction of the esterification catalyst is also carried out continuously. Similar considerations apply to batchwise operation.

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Mixing apparatus preferably used are stirred vessels equipped with drive systems having stepless control, for example blade stirrers, which give homogeneous mixing.

15 The average residence time in the mixing apparatus is from 0.5 to 45 minutes, preferably from 10 to 20 minutes.

Prior to the gravitational phase separation, the crude ester preferably has from 0.1 to 5% by weight content of monosalt of 20 dicarboxylic half-ester.

The subsequent gravitational phase separation may use vertical phase separators, since the removal of the solids here (e.g. titanium hydroxide) by separation is particularly simple.
25 However, horizontal phase separators may also be used, since the titanium hydroxides sediment rapidly and completely in the aqueous phase, normally without forming any solids-containing intermediate layer out of crude ester, aqueous phase, and titanium hydroxide particles which is difficult to separate.
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The phase separation times for the liquid/liquid separation and for the solid/liquid separation are generally in the range from 5 to 30 minutes.

35 The organic phase removed by separation and substantially composed of the diester and unreacted esterification alcohol is then further purified in a manner known per se to the skilled worker, for example by stripping.

40 The aqueous phase removed by separation normally comprises most of the monosalt of dicarboxylic half-ester.

One advantage of the process of the invention is that the phase separation generally takes place rapidly and without disruption 45 (without formation of solids-containing intermediate layers and emulsions).

A particular advantage is that the plasticizer esters are free
from solids when they pass into the downstream stages of the
process. This can give an increase in the operating times of the
apparatus used, by a factor of from 10 to 20.

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The economic advantages of working the process of the invention
on an industrial scale are an increase in capacity in the stages
of the process for crude ester treatment, and also an increase in
availability and operating reliability. The reduction in the

10 number of purification phases considerably reduces the
maintenance costs for the plants used and cuts plasticizer ester
losses.

Examples

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Example 1

180 g of crude diisononyl phthalate (prepared as in
DE-A 197 21 347) were thoroughly mixed for 5 minutes in a

20 separating funnel with 20 g of water and 0.4% by weight, based on
the mixture, of the monosodium salt of monoisononyl phthalate.
The resultant mixture had a milky cloudiness, and there was no
remaining detectable phase boundary. 3% by weight, based on the
mixture, of a 0.5 millimolar aqueous solution of aluminum sulfate

25 were then added to the mixture, and the entire mixture was again
vigorously mixed. After standing for ten minutes, there was a
clearly discernible phase boundary between the two different
cloudy phases.

30 Example 2

A stable emulsion from a production plant with 24% by weight of
water of pH 9.8, 2.5% by weight of isononanol, and 73% by weight
of diisononyl phthalate, and also 0.5% by weight of monosodium

35 salt of monoisononyl phthalate, was treated with 8% by weight,
based on the mixture, of a 0.5 millimolar aqueous solution of
aluminum sulfate, and vigorously mixed. After standing for ten
minutes, a phase boundary was clearly discernible between the two
different phases.

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Example 3

Each of three shaking funnels (shaking funnels 1, 2 and 3) was
charged with 25 ml of water and 250 g of diisononyl phthalate,

45 and 0.2 g of the monosodium salt of monononyl phthalate was added
to each shaking funnel. All three of the shaking funnels were
then shaken vigorously. There was then no remaining phase

boundary, and in all three cases the product was a stable
emulsion. The subsequent procedure was as follows:

Shaking funnel 1: After 1 h 30 min, a white emulsion remained,
5 but about 5 ml of aqueous phase had separated out at the bottom.

Shaking funnel 2: 5 ml of a 10 millimolar calcium chloride
solution were added, and the contents of the shaking funnel were
again mixed. After 15 min, relatively large droplets formed
10 toward the based. After 1 h, 30 ml of aqueous phase had separated
out. Above the phase boundary there was a white non-transparent
layer of thickness from 8-10 mm, while the rest of the organic
phase was transparent, although cloudy. After 1 h 30 min, no
further change was detectable.
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Shaking funnel 3: 30 ml of a 10 millimolar calcium chloride
solution were added and the contents of the shaking funnel were
again mixed. After 15 min, a clear phase boundary was detectable.
After 30 min, 55 ml of aqueous phase had separated out. There was
20 a sharp phase boundary – without any sign of emulsion.

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